Oxalate-promoted formation of saponite at 60°C and 1 atm pressure

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Introduction and Results

In carbonaceous chondrites there is a strong correlation between the occurrence of clay minerals and the presence of polar organic molecules (*e.g.* oxalic acid) [1][2]. Oxalic acid in the aqueous alteration phase of these meteorites could have enhanced the alteration of olivine and orthopyroxene to form Mg- and Fe-rich phyllosilicates [2]. It has also been proposed that clay minerals might have caused an enrichment of chiral "left"-handed amino acids like isovaline in these meteorites [3]. It is therefore important from the point of view of prebiotic chemistry whether oxalic acid might have catalyzed the formation clay minerals.

In this study we tested whether oxalate catalyses the crystallization of saponite from a silica gel powder at 60°C and ambient pressure. For comparison in a second experiment NaOH solution was used instead of oxalate. Low magnification TEM images showed clusters of well developed globular aggregates consisting of packets of saponite crystals in the oxalate experiment and poorly crystallized saponite from the NaOH solution. High-resolution TEM lattice-fringe images of the ultrathin sections of the saponite globules treated with octadecylammonium (n_C=18) cations revealed the presence of 2:1 layer structures having variable interlayer charges: (1) short sequences of low-charge 2:1 silicate layers with an interlayer spacing of 13 to 14 Å and (2) sequences of higher charge 2:1 silicate layers having highly expanded interlayers of 25 to 33 Å. The difference in interlayer expansion results from the variation in the substitution of Al^{3+} for Si^{4+} within the tetrahedral sheets of the saponite crystallites. The Si/Al ratio seems to be passed on from layer to layer by heritage which is demonstrated by the regular interlayer expansion within the packets.

Conclusions

This study (i) showed the strong catalytic effect of oxalate on the nucleation and growth of saponite at low temperatures and pressure in contrast to NaOH, (ii) established the composition and structure of the 2:1 silicate layers of the saponite, and (iii) evaluated the replicating capability of the saponite. This study does not only offer an explanation for the formation of clay minerals in carbonaceous chondrites but may also explain the origin of clay minerals in other systems that contain oxalic acid associated with endolithic and epilithic (*e.g.* lichen) communities.

[1] Becker & Epstein (1982) *GCA* **46**, 97-103. [2] Hartman *et al.* (1993) *Origins of Life and Evolution of Biosphere* **23**, 221-227. [3] Pizzarello *et al.* (2003) *GCA* **67**, 1589-1595.

Transformations of mercury, arsenic and selenium in river sediments contaminated with coal ash: Field and laboratory studies

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Coal combustion products, including coal ash, represent the largest industrial waste stream in the United States and contain elevated levels of toxic elements such as mercury (Hg), arsenic (As), and selenium (Se). Much of this waste is stored in unlined holding ponds and landfills that are not always monitored for their discharge to adjacent waters. Moreover, these holding ponds are susceptible to failures such as the disaster at the Tennessee Valley Authority (TVA) Kingston Fossil Plant in 2008 that caused more than 1 billion gallons of coal ash slurry to spill into the adjacent Emory River. In such cases, the fate of toxic elements associated with coal ash is greatly influenced by environmental conditions such as redox potential and microbial activities that induce transformations and leaching of contaminants. Here, we investigated the mobilization of coal ash contaminants in sediments through a field study of the river system surrounding the TVA coal ash spill site and also through laboratory sediment slurry experiments to understand how river conditions could facilitate mobilization of trace elements and production of methylmercury (MeHg). In the field survey, we sampled the sediments and surface water at the spill site during a two year period after the spill event. The results indicated elevated levels of MeHg in the river sediments near the spill site. The mercury originating from the coal ash demonstrated a stable Hg isotope signature that was different from the mercury originating from historical sources to this ecosystem. Thus, the isotope data suggested that the coal ash was stimulating MeHg production in the river sediments near the TVA site (either by providing Hg or other substrates for methylating bacteria). In the laboratory experiments, we cultured anaerobic sediment slurries to determine how the addition of coal ash could influence porewater chemistry and Hg speciation. The microcosms were prepared using sediment and surface water from a location several miles upstream of TVA spill site and cultured in an anaerobic chamber. A selection of the slurries was amended with coal ash obtained from the TVA Kingston Plant. Preliminary results of the sediment slurry incubations showed that the coal ash increased the amount of dissolved As and Se in the slurries at the initial time point. Over 4 days of incubation, dissolved As continued to increase while dissolved Se decreased in the slurries. These results suggested that arsenic was converting from As(V) to more soluble As(III) species in the slurries while selenium was converting from oxidized forms (e.g. selenate or selenite) to less soluble, reduced forms (e.g. elemental Se, selenide). The concentration of dissolved sulfate also decreased during the experiment, consistent with low redox potential in the slurries. While MeHg was observed in all slurry samples, the effect of coal ash on Hg speciation was mixed, with the coal ash providing a stimulating effect for MeHg production in some slurries and no effect in others. Further work will include sediment-coal ash slurries with more active microbial growth conditions. Overall, our field and laboratory studies highlight the need to consider environmental conditions in assessing the potential hazards of contaminants associated with coal ash.